XVIII. *An Account of some Experiments on different Combinations of Fluoric Acid. By* John Davy, *Esq. Communicated by Sir* Humphry Davy, *Knt. LL.D. Sec. R. S.*

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Introduction.

Two years ago, I engaged, at the request of my brother, Sir H. Davy, in an inquiry respecting the nature of common fluoric acid gas. My principal object was to ascertain whether silex is essential to its constitution, and whether the proportion is constantly the same. This subject, and experiments on the fluoric and fluoboracic acids, occupied me for about six months. Since that time, the work of M. M. Gay Lussac and Thenard has appeared, entitled "Recherches Physico-Chemiques," in the second volume of which is an elaborate dissertation on fluoric acid. These philosophers, I find, have anticipated many of my results, and consequently very much abridged my labour of detail in the following pages. To repeat what is already known would be useless, I shall therefore confine myself to describe what I have observed, which appears to me yet novel, or different from the observations of the French chemists. The order which I shall pursue, will be that which I observed in my experiments. I shall divide what I have to advance into four parts. The first part will relate to the silicated fluoric acid gas, and to the subsilicated fluoric acid; the second to the

combinations of these acids, and of pure fluoric acid with ammonia; the third to fluoboracic acid; and the fourth to its ammoniacal salts.

SECT. 1. *On silicated fluoric acid Gas, and subsilicated fluoric Acid.*

The facts which have already been published by M. M. GAY LUSSAC and THENARD and others, appear to me to be sufficient to prove that pure fluoric acid has not yet been obtained in the gaseous state, and that silex, or boracic acid, is requisite that it may assume this form. Were more evidences necessary, I could advance many in point. One circumstance only I shall mention, proving that common fluoric acid gas is perfectly saturated with silex. I have preserved this gas, made by heating, in a glass retort, a mixture of fluor spar and sulphuric acid, for several weeks over mercury in a glass receiver uncoated with wax, without observing the slightest erosion to be produced.*

This gas, with great propriety, has lately been called silicated fluoric. Before I proceed to its analysis, I shall notice what method I have found the best for obtaining it. I have, for a considerable time, long before M. M. GAY LUSSAC and THENARD'S work was published, added to the mixture of fluor spar and sulphuric acid, a quantity of finely pounded glass, and have thus procured the gas with the greatest facility. The advantages of this addition are considerable. The retort is saved, which otherwise, in less than one operation, would be

* The sides of the receiver indeed became obscure; but this was not from erosion, but from deposition, as appeared from the transparency and polish of the glass being readily restored by slight friction. What the deposition was, I am ignorant of. After several weeks it was so trifling, as to give only a slight degree of opacity to the receiver.

destroyed; and a much larger quantity of gas is procured from the same materials, and with less trouble and less heat; the action indeed at first is so powerful, that gas begins to come over before the application of heat is made, and a very gentle one only is required to continue its production.

Previous to its analysis, it was necessary to ascertain the specific gravity of the gas. This I have endeavoured to do. The gas, the subject of experiment, was quite pure, being totally condensed by water. A Florence flask was exhausted; in this state, weighed by a very delicate balance, it was

	= 1452.2 grains.
Filled with common air -	= 1452.2 + 10.2
Again exhausted - -	= 1452.2
Filled with silicated fluoric gas	= 1452.2 + 36.45

Hence as 10.2 : 31 : : 36.45 : : 110.78.

Thus it appears, that 100 cubic inches of silicated fluoric acid gas, at ordinary temperature and pressure, are equal to 110.78 grains.

When silicated fluoric acid gas is condensed by water, it is well known that part only of the silex is deposited. To obtain the whole, in order to ascertain the proportion in the gas, I have employed ammonia in excess. 40 cubic inches of the gas (barom. 30, therm. 60) were transferred in portions of 10 cubic inches, at a time to a solution of ammonia. The silex precipitated was carefully collected on a filter, and washed till the water that passed through it, ceased to be affected by nitrat of lime. It was next dried, and strongly heated in a platina crucible. It weighed 27.2 grains, and was pure silex. Supposing fluoric acid to be the remaining 17.1 grains, which added to 27.2 grains are equivalent to the weight of 40 cubic

inches of the gas, it appears that 100 parts by weight of this gas consist of

61.4	silex
38.6	fluoric acid
100.0	

That this estimate may be correct, it is evident, that ammonia should have the property of precipitating the whole of the silex of silicated fluoric gas; which I shall not now endeavour to prove, but leave it to be considered in another part of the paper.

There is no improbability attached to the idea, that silicated fluoric acid gas may, from the manner in which it is prepared, contain a proportion of alkali. To discover whether this was the case, a solution of nitrat of lime was added to the ammoniacal solution neutralized by nitric acid, from which the silex in the preceding experiment had been removed. The precipitate of fluat of lime was separated by filtration. The filtered liquid was evaporated to dryness; and the ammoniacal salt heated in a platina crucible till it was entirely dissipated. The residue had the appearance and taste of quick lime. It was dissolved in acetic acid, and the solution yielded sulphat of lime on the addition of sulphat of ammonia. The liquid was evaporated to dryness, and when the residuum had been heated to dull redness, nothing remained but a little white powder, weighing about a grain, and having all the properties of gypsum. Thus it appears that silicated fluoric acid gas contains no alkali.

My next object was to ascertain the composition of common liquid fluoric acid—that acid obtained by the decomposition of

silicated fluoric acid gas by water, and which, on account of the separation that occurs of part of the silex, may, with greater propriety, be called subsilicated fluoric acid. For this purpose, 43.21 cubic inches, barom. 30.4, therm. 50, or 44 cubic inches at common temperature and pressure, were successively added, two cubic inches at a time, to one cubic inch of distilled water in a small jar over mercury. The whole of this, the gas being pure, was readily condensed. The temperature was somewhat raised. The silex precipitated, formed a gelatinous mass of a blueish colour, which had absorbed all the water like a sponge, so that none appeared fluid. This gelatinous mass was carefully transferred to a filter, and washed with distilled water till it was rendered insipid and incapable of reddening litmus paper. It retained its blueish hue only whilst moist. When dried and ignited, it was in thin lamellæ, and of a snow-white colour, and surprisingly bulky. It weighed 7.33 grains, and was found to be pure silex. Thus it appears that the subsilicated fluoric acid formed by the decomposition of 44 cubic inches of silicated fluoric acid gas contains 7.33 grains of silex less than the gas itself. Consequently independent of water, which no doubt is essential to this acid, 100 parts of it seem to consist of

54.56	silex
45.44	acid
100.00	

I have endeavoured to ascertain what quantity of silicated fluoric acid gas a given quantity of water will condense. In one instance $\frac{19}{100}$ of a cubic inch of distilled water absorbed 51 cubic inches, barom. 30.5, therm. 60. The gas was added to

the water in a jar over mercury, as fast as it was absorbed. The experiment was stopped, when the gas, after having remained in contact with the water a whole night, ceased to be diminished. According to this result, the proper correction being made for the additional pressure, water decomposes about 263 times its bulk of silicated fluoric acid gas.

Dr. PRIESTLEY observed, that muriatic acid gas reproduced silicated fluoric gas from the crust of silex formed, when the latter is condensed by water.* This experiment I have repeated, and as it appears to show more correctly the quantity of gas water can condense, I shall describe the result. 2.4 cubic inches of muriatic gas were added to a drop of water, that had previously absorbed one cubic inch of silicated fluoric gas, in a jar over mercury. There was an immediate absorption equal to $\frac{2}{10}$ of a cubic inch. The mixture of silex and subsilicated fluoric acid effervesced, and from an apparent solid became fluid, the whole of the silex gradually disappearing. After the first mentioned absorption, there was no farther. The gas produced was silicated, as appeared from the crust it deposited when removed to water, and the liquid formed was pure muriatic acid, for decomposed by concentrated sulphuric, it afforded merely muriatic acid gas, without any silicated fluoric. The evident conclusion from the preceding result is, that water condenses equal quantities of the muriatic and silicated fluoric acid gasses, and consequently that the first estimate is too low, and instead of 263 times its bulk, it is probably more correct to say that water to be saturated requires at least 365 times its volume. Neither will this estimate appear inconsistent with the former result, when the

* Vide PRIESTLEY on Air, Vol. II. p. 202.

deposition of silex is considered as an obstacle to the free exposure of the surface of the water to the gas.

Subsilicated fluoric acid is decomposed by ammonia and the fixed alkalies, and by all the earths that I have made trial of. It is also decomposed by the sulphuric acid and the boracic, as well as by the muriatic acid gas.

Of the particular changes which occur when it is acted upon by the alkalies, I defer giving any account at present, as it is my intention to do it in the next section.

To learn the effect of heat on it, a small quantity of strong acid, pure and transparent was introduced into a retort connected with mercury. A spirit lamp being applied about three cubic inches of silicated fluoric acid gas were produced. The neck of the retort was lined with silex in a gelatinous state, and much liquid subsilicated fluoric acid, that had distilled over, was condensed in the colder part of the neck, and was absorbed by bibulous paper previously introduced, to prevent the distilled fluid from entering the jar for the reception of the gas. When the whole of the acid in the bulb of the retort had been evaporated, little or no silex remained.

The general result of this experiment is very different from that which Dr. PRIESTLEY, who first made it, obtained. Instead of silicated fluoric acid gas, he procured " vitriolic acid air," sulphureous acid gas.

I have tried also the effect of heat on the silicious crust, formed by the decomposition of silicated fluoric acid gas, by water; but could obtain no sulphureous acid gas, as Dr. PRIESTLEY did only a small quantity of silicated fluoric.

The correctness of Dr. PRIESTLEY's observations cannot be doubted. I can only account for his results, by supposing that

some sulphuric acid in consequence of the high temperature employed in making the gas was volatilized, and mixed with the subsilicated fluoric acid, and that mercury also was present from the acid being prepared over this metal.

These experiments too oppose another statement relative to a method prescribed for making fluoric acid gas free from silex, by merely heating strong subsilicated fluoric acid in a retort, and collecting the gas over mercury. It is asserted, in chemical works of some reputation, that this process is successful. I have never found it so, having always obtained results similar to those above stated. This, I suppose, is one of the many errors that have secretly crept into repute, and has been believed, because never subjected to the test of experiment.

The action of concentrated sulphuric acid on subsilicated fluoric acid, is similar to that of muriatic acid gas, occasioning a disengagement of silicated fluoric acid gas. Facts which appear to prove, that water is absolutely essential to the existence of this acid.

Boracic acid decomposes it, in a very different way, not from any predominant affinity for the water, but in consequence of a stronger attraction for the fluoric acid itself. Silicated fluoric acid of course is not produced ; but liquid fluoboracic acid and the silex is precipitated in a gelatinous state, as when ammonia is employed.

These are the principal facts I have to notice respecting this acid. Before I conclude, I shall briefly mention a few other circumstances. Applied to the tongue, in its concentrated state, it produces a very painful sensation, like that which strong muriatic acid does, and it has a very similar effect on the cuticle. It does not appear to erode glass, for I have kept it in

bottles of this substance more than a month without any action being perceptible. Exposed to the air, it slowly and almost completely evaporates, there being only a very trifling silicious residue; and when gently heated in an open vessel, it is rapidly dissipated in white fumes.

SECT. II. *On the Combinations of silicated fluoric acid Gas, and the subsilicated Fluoric, and the fluoric Acids with Ammonia.*

M. GAY LUSSAC has shewn that silicated fluoric acid gas, like carbonic acid gas, condenses twice its volume of the volatile alkali.* The experiment I have several times repeated, and constantly with the same result, no difference appearing when the acid gas was added in great excess to the alkaline, or the alkaline to the acid. This being the case, and knowing the specific gravities of the two gasses,† 100 parts by weight of silicated fluat of ammonia seem to consist of

24.5	ammonia
75.5	acid
100.0	

Silicated fluat of ammonia volatilizes unaltered, if heated by a spirit-lamp in the vessel in which it is formed, and provided moisture be entirely excluded.

Like silicated fluoric acid gas itself, this salt is decomposed by water, and a similar precipitation of silex occurs, and in the same proportion. Thus the salt formed by the union of 30

* Vide Mém. d'Arcueil, Tom. II.

† According to Sir H. DAVY, 100 cubic inches of ammonia, barom. 30, therm. 60, weigh 18 grains. It is this estimate which I have taken.

cubic inches of silicated fluoric gas, and 60 of volatile alkali (barom. 30, therm. 60) in a small glass jar over mercury, being carefully collected and introduced into water, afforded five grains of pure silex, weighed after being well washed and heated to redness.

The saline solution, since part of the silex of the silicated fluoric acid gas is separated during its production, appears to be a subsilicated fluat, or a combination of subsilicated fluoric acid and ammonia. Another mode of making it, more directly proves that this is its composition. When ammonia is added to the subsilicated fluoric acid in excess, this salt is formed without any precipitation. From these facts, it may be concluded, that independent of water, which appears to be essential to its existence, 100 parts of it consist of

28.34 ammonia
71.66 acid

100.00

Subsilicated fluat of ammonia has a pungent saline taste. It just perceptibly reddens litmus paper. Slowly evaporated, it forms small transparent and brilliant crystals. The largest I could obtain, appeared to be tetrahedral prisms. The solid salt is very soluble in water; but is not deliquescent. When heated it appears to sublime unaltered. It is curious that the solution of this salt, when evaporated by a heat near its boiling point, powerfully erodes the glass or porcelain vessel, and a residuum of silex appears, on the addition of water, to redissolve the salt. This erosion and residue of silex I have seen produced three times following, with the same quantity of salt. I mention the fact, which, I believe, was before observed by SCHEELE, without

attempting an explanation of it. It may perhaps be said, that as the water evaporates, the affinity of the subsilicated fluat for silex increases.

Subsilicated fluat of ammonia is decomposed by the sulphuric acid, and by muriatic acid gas, and also by the fixed alkalies and by ammonia.

Sulphuric acid expels from it, silicated fluoric gas and hydrated fluoric acid fumes.

Muriatic acid gas acts slowly on it, and effects its decomposition apparently through the medium of its water. A little of the crystalline salt was introduced into muriatic acid gas in a jar over mercury. In a short time some silicated gas was produced, as the silicious deposition, on the addition of water, indicated. Strong muriatic acid was substituted for the acid gas. Now no apparent change took place, for on evaporating the acid, the residue, decomposed by sulphuric acid, afforded only silicated fluoric acid gas.

The alkalies form by the decomposition of this salt, the same compounds that they do by their action on subsilicated fluoric acid.

Potash expels the ammonia, and produces the silicated fluat and fluat of potash, as M. M. Gay Lussac and Thenard have described.

The changes occasioned by soda appeared to me similar; but the gentlemen just mentioned, assert that this alkali precipitates the whole of the silex, and does not form a triple salt with it and part of the acid.

Ammonia seems to me to separate completely the silex, and by uniting with the pure acid to constitute a true fluat. MM. Gay Lussac and Thenard are of a different opinion. They

say that the whole of the silex cannot by this method be removed, but only the principal part. Their reason for this belief, is, that on repeatedly evaporating the salt after the addition of ammonia and redissolving it, they have each time observed a residue of silex. If they employed metallic evaporating vessels, the results of my experiments do not agree with theirs; for making use of platina for this purpose, and adding an excess of ammonia, I never detected traces of silex on evaporating the filtered fluat. But our results agree, if they employed glass or porcelain vessels, which fluat of ammonia has the property of corroding.

I now proceed to the consideration of fluat of ammonia; but before I describe some of the properties of this fluat which I have observed, I shall briefly mention the means pursued for ascertaining the proportions of its constituent parts.

The composition of subsilicated fluat of ammonia being known, that of the fluat (granting what is already advanced respecting its formation to be correct) may be inferred from the proportion of silex, that a given quantity of ammonia will precipitate. 18 cubic inches of ammoniacal gas were condensed by $\frac{1}{4}$ of a cubic inch of distilled water in a small glass tube over clean mercury. This ammoniacal solution was added to a clear filtered solution of subsilicated fluat of ammonia. A precipitate of silex was immediately produced. After several hours standing, this precipitate was collected on a filter, well washed and dried and heated to redness. It was pure silex, and weighed 1.6 grains. This experiment, like all the preceding, was repeated, and the result confirmed. In both instances there was an excess of subsilicated fluat. The precipitations were made in a platina vessel, and the solutions were neither heated before or after

the separation of the silex. Calculating from this result, 100 parts of fluat of ammonia seem to consist of

76.4	ammonia
23.6	fluoric acid
100.0	

Water appears to be a constituent part of this salt.

It may be rendered neutral by means of a gentle heat, which expels the excess of ammonia employed in its formation. In its neutral state, it has a strong saline taste, and it readily deliquesces when exposed to the atmosphere. Like the neutral carbonats, it is decomposed by heat; but there is this difference between them, part of the pure alkali is expelled instead of the acid, and an acid fluat of ammonia is formed. A gentle heat only is required for the purpose, that of boiling water is nearly sufficient. When the heat is much stronger, the salt fuses and passes off in dense fumes of a most peculiar suffocating odour. The effects of these fumes, when inhaled, are very powerful and disagreeable, and even dangerous, I might venture to say, were I to speak from my own experience. In one instance, when I inhaled only a small quantity, they produced in a few minutes a violent cough and catarrh, and apparent accumulation of blood in the neck and head, and symptoms altogether not unlike those the attendants of apoplexy, which continued for about a quarter of an hour, and then slowly diminished, and gradually disappeared without leaving any permanent bad effect. The fluat of ammonia, when heated in a metallic vessel, appears to sublime unaltered. But the result is different when the experiment is made in a glass one. Ammonia is expelled, the glass is corroded, and subsilicated fluat

of ammonia is formed and sublimed. Its action on glass is so powerful, that I have successfully employed it instead of fluoric acid itself, for etching on this substance. It has one advantage, that it is more manageable. The solution may be applied by means of a hair pencil or a common pen to the glass, and the erosion will be produced by exposure to a moderate temperature.

The fixed alkalies, and all the earths that I have tried, decompose this salt; they expel the ammonia, and form true fluats with the acid itself. I have examined all the fluats thus formed, and have endeavoured to ascertain the proportions of their constituent parts; but I am not sufficiently satisfied of the accuracy of the results, to venture to give an account of them.

SECT. III. *On Fluoboracic Acid Gas.*

MM. GAY LUSSAC and THENARD, who first discovered this gas, obtained it by heating strongly, in an iron tube, a mixture of fluor spar and fused boracic acid. I have found that it may be more easily procured, in greater abundance, and at less expence, by gently heating, in a common glass retort, a mixture of finely pounded boracic acid * and fluor spar with concentrated sulphuric acid. 1 part by weight of fused boracic acid, 2 parts of fluor spar, and about 12 of sulphuric acid appear to be the proportions best adapted for the purpose. This method will require no explanation when it is considered that boracic acid, as has already been observed, precipitates silex from liquid subsilicated fluoric acid. If the heat is gentle, not

* Common calcined borax answers the same end, but no so well. Its only recommendation to preference is cheapness.

nearly sufficient to occasion the ebullition of the sulphuric acid, and the proportions just recommended are used, the retort will not be injured, and pure fluoboracic acid gas will be produced in abundance. When the gas ceases to come over, if the heat is raised, more will be evolved, and there will be distilled over at the same time, a viscid fluid, which is a compound of sulphuric acid and fluoboracic acid gas. Now the operation should be stopped, if the object is to obtain merely pure fluoboracic gas, a long continuation of the heat producing some silicated fluoric. Before quitting the subject, it should be observed that the quantity of sulphuric acid employed is of considerabl consequence to the success of the experiment. If too much is used, there is a great loss of gas from the property which sulphuric acid has of absorbing fluoboracic acid gas; and if too little is employed, it soon becomes diluted, and loses the power of generating the gas, though it may still decompose the fluor spar. Both extremes, therefore, are to be avoided, and the proportion of acid mentioned above, as far as my experience goes, appears to be the best.

I have endeavoured to ascertain the specific gravity of fluoboracic gas.

The flask exhausted weighed	1400.5 grains.
Filled with common air -	1400.5 + 6.2
Again exhausted - -	1400.5
Filled with pure acid gas -	1400.5 + 14.7.

Thus it appears that 100 cubic inches of fluoboracic gas are equal to 73.5 grains.

MM. GAY LUSSAC and THENARD have described the compound of this gas and water, a fuming fluid, in many respects similar to concentrated sulphuric acid. Like this acid, I have

observed that it possesses a slight degree of tenacity, so that it has an oily appearance when poured from one vessel to another; and similar in another respect, it possesses the property of charring animal and vegetable substances, and which the French chemists observed belonging to the gas itself. I have found that water condenses more of this, than it does of any other known gas, no less than 700 times its volume. The experiment was then made, barom. 30.5, therm. 50, $\frac{14}{100}$ of a cubic inch of water were introduced into a tube over mercury, and the gas, in portions of 5 cubic inches at a time, was added until 100 cubic inches had been absorbed, when the water was apparently saturated. This acid was of the specific gravity 1.77.

The property which sulphuric acid has of absorbing fluoboracic acid gas has already been noticed. I found that $\frac{1}{2}$ cubic inch of sulphuric acid, of the specific gravity 1.85, condensed 25 cubic inches of the gas, or 50 times its volume. The compound acid was strongly fuming, and appeared more tenacious than pure sulphuric acid, yet not nearly so much so as that compound of the two which distills over during the latter part of the operation of making fluoboracic gas.

This latter compound has some peculiarities. It is so tenacious, that it flows very slowly. It appears to be far more volatile than pure sulphuric acid. When poured into water, a dense white precipitate is formed, the exact nature of which I have not yet satisfactorily ascertained; but which is not produced by the direct compound of sulphuric acid, and the fluoboracic.

Sect. IV. *On the Combinations of fluoboracic acid Gas, and ammoniacal Gas.*

M. Gay Lussac has combined fluoboracic acid gas with ammonia. He states, that equal volumes of the two gasses condense each other.* This I have found to be the case, and I have also found that fluoboracic acid gas condenses twice, and even three times its volume of the volatile alkali. The compound observed by M. Gay Lussac is solid, white, and opaque, like the ammoniacal salts. The combinations I have obtained are liquid, transparent, and colourless, like water, though they are entirely free from this fluid. They were made by the direct union of the two gasses. 5 cubic inches of ammoniacal gas were added to the same volume of the fluoboracic gas contained in a small jar over dry mercury. There was a complete condensation of both, and the solid salt was the result. 5 cubic inches more of ammonia were introduced. The whole was quickly absorbed, and the solid salt was converted into the transparent fluid. 5 cubic inches more were added, which too were slowly absorbed, but without any change of form.

The solid salt volatilizes in close vessels unaltered, on the application of a gentle heat.

Both fluid compounds, when heated, are rendered solid, from the expulsion of part of the ammonia. Exposure to the air is attended with the same change, and the same effect is produced by the muriatic and carbonic acid gasses.

Knowing the volumes of the acid, and alkaline gasses which

* Vide Mém. d'Arcueil, Tom. II.

combine, it is easy to calculate the proportions of each by weight in the respective salts.

100 Parts consist of	Ammonia.	Acid.
The solid compound	19.64	80.32
The first fluid -	32.9	67.1
The second fluid	42.4	57.6

These combinations are curious in many points of view. They are the first salts that have been observed liquid, at the common temperature of the atmosphere, without containing water. And they are additional facts in support of the doctrine of definite proportions, and of the relation of volumes.